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Crystal structure of 8,10-diiodo-3-(iodomethyl)-2,3-dihydro-[1,4]oxazino-[2,3,4-*ij*]quinolin-4-ium triiodide, $[C_{12}H_9I_3NO]\cdot I_3$, $C_{12}H_9I_6NO$

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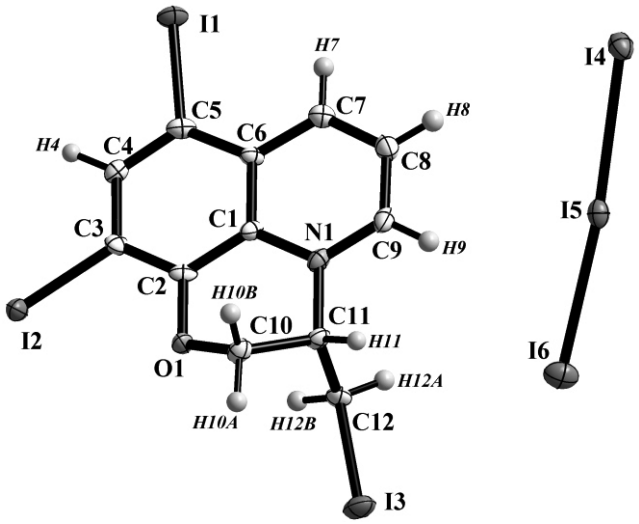

Abstract

$C_{12}H_9I_6NO$, monoclinic, $P2_1/n$ (no. 14), a = 9.2855(2) Å, b = 17.1834(4) Å, c = 12.2416(3) Å, β = 93.258(2)°, V = 1950.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.0433, $wR_{ref}(F^2)$ = 0.0630, T = 120 K.

Table 1. Data collection and handling.

Crystal:	brown rhombohedrals, size 0.0131×0.0460×0.0846 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	95.53 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Ruby, Gemini, ω
$2\theta_{max}$:	62.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17314, 5893
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4561
$N(param)_{refined}$:	181
Programs:	CrysAlis PRO [10], SIR92 [11], SHELX [12], DIAMOND[13], WinGX [14], enCIFer [15]

Source of material

5,7-diiodo-8-(allyloxy)quinoline was obtained using 5,7-diiodo-8-quinolinol and allyl bromide in acetone/K_2CO_3 with reflux. The solution of 5,7-diiodo-8-(allyloxy)quinoline (0.110 g, 0.25 mmol) in 10 ml of acetone was mixed with a solution of iodine (0.192 g, 0.75 mmol) in 10 ml of acetone. Single crystals for the X-ray diffraction study were obtained after keeping the resulting mixture at room temperature in closed flask for 5 days and then by slow solvent evaporation, yield: 0.135 g (57%).

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Experimental details

The positions of the H atoms were calculated based on geometric criteria (C–H = 0.97 Å, 0.93 Å and 0.85 Å for methylene, aromatic and methine atoms, respectively) than have been placed in their calculated position and refined isotropically using a rider model with U_{iso}(H) = 1.2U_{eq}(C).

Discussion

A number of synthesis for quinoline compounds with fused N-1/C-8 centers [1-3] and X-ray structures of condensed tricyclic azines [4-5] were reported. Represented crystal structure can be an interesting object for studying the directed self-assembly of poliyodide chains [6-8]. The asymmetric unit of the title compound consists of one iodoquinolinium derivative cation and one triiodide anion. The atoms N1 and C1-C9, defining the quinolinium part of molecular cation, are situated in the same plane. The C–C bonds lengths range from 1.363(7) to 1.423(7) Å; the C–N bond distances range from 1.339(7) to 1.382(6) Å. The I1 and I2 atoms are located in the same plane as the quinolinium moiety with C5–I1 and C3–I2 bond distances of 2.090(5) and 2.091(5) Å, respectively. The crystal structure confirms the closure of the six-member ring between O1 and N1, during cyclization reaction, resulted in C11–N1 bond formation. The C11–N1 bond has a covalent character (1.493(6) Å). For six-membered folded ring the C–O bond distances range from 1.351(6) to 1.432(6) Å, and C10–C11 bond length is 1.507(7) Å. In this ring the C10 atom of methylene group is significantly out of plane (24.2°). The exoclyclic C11–C12 bond has a single bond character at a bond distance of 1.525(7) Å. The C12–I3 bond length is 2.146(5) Å and significantly deviated from mean plane of iodoquinolinium moiety (30.9°); the C11–C12–I3 angle is 110.5(3)°. The molecular conformation is established by intramolecular contacts C12–H12B···O1 and C10–H10A···I3 with D···A distances 2.955(6) and 3.524(5) Å, respectively. The triiodide anion is almost linear with I4–I5 and I5–I6 distances of 2.9493(5) and 2.8918(5) Å, respectively, and I4–I5–I6 angle is 172.954(17)°. The crystal packing of title compound is stabilized via multiple intermolecular contacts between $[C_{12}H_9I_3NO]^+$ cation and iodine atoms that can be attributed to halogen bonding [9].The inversely oriented organic cations are linked through I1···I2' (3.8718(5) Å; ' = –x+1, –y+1, –z) intermolecular contacts forming dimeric structure associations. Additionally, these dimers are extended along a-axis direction through I2···I4' (3.4947(5) Å; ' = –x+1, –y+1, –z) contacts. Finally, the overal packing is completed by intermolecular contacts C10–H10B···I4' (3.1625(4) Å; ' = –x+1, –y+1, –z) and C10–H10B···I6' (3.1376(4) Å; ' = x–½, –y+½+1, +z–½).

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4)	4*e*	0.5307	0.5802	0.0045	0.019
H(7)	4*e*	1.0081	0.6186	0.1353	0.023
H(8)	4*e*	1.1518	0.7264	0.1567	0.026
H(9)	4*e*	1.0636	0.8470	0.1047	0.024
H(10A)	4*e*	0.6661	0.9312	–0.0950	0.023
H(10B)	4*e*	0.7506	0.8581	–0.1344	0.023
H(11)	4*e*	0.8952	0.9226	–0.0027	0.019
H(12A)	4*e*	0.8222	0.9250	0.1835	0.023
H(12B)	4*e*	0.6653	0.9037	0.1386	0.023

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.7782(5)	0.7490(3)	0.0389(4)	0.015(3)	0.012(3)	0.019(3)	–0.001(2)	0.005(2)	–0.001(2)
C(2)	4*e*	0.6375(6)	0.7601(3)	–0.0089(4)	0.019(3)	0.014(3)	0.014(3)	0.005(2)	0.008(2)	0.002(2)
C(3)	4*e*	0.5465(5)	0.6970(3)	–0.0204(4)	0.011(2)	0.019(3)	0.021(3)	0.003(2)	0.004(2)	–0.001(2)
C(4)	4*e*	0.5938(5)	0.6221(3)	0.0120(4)	0.019(3)	0.014(3)	0.014(3)	–0.002(2)	0.004(2)	0.000(2)
C(5)	4*e*	0.7311(6)	0.6105(3)	0.0544(4)	0.022(3)	0.015(3)	0.020(3)	0.004(2)	0.006(2)	0.002(2)
C(6)	4*e*	0.8286(5)	0.6738(3)	0.0711(4)	0.015(3)	0.012(3)	0.018(3)	0.002(2)	0.004(2)	0.004(2)
C(7)	4*e*	0.9718(6)	0.6672(3)	0.1148(4)	0.020(3)	0.018(3)	0.020(3)	0.002(2)	0.003(2)	0.001(2)
C(8)	4*e*	1.0577(6)	0.7312(3)	0.1272(4)	0.018(3)	0.026(3)	0.021(3)	0.001(2)	–0.002(2)	–0.002(2)
C(9)	4*e*	1.0045(6)	0.8035(3)	0.0960(4)	0.019(3)	0.020(3)	0.021(3)	–0.004(2)	0.002(2)	–0.007(2)
C(10)	4*e*	0.7049(6)	0.8809(3)	–0.0726(4)	0.024(3)	0.015(3)	0.017(3)	–0.002(2)	–0.001(2)	0.002(2)
C(11)	4*e*	0.8149(6)	0.8912(3)	0.0215(4)	0.021(3)	0.010(3)	0.018(3)	0.000(2)	0.000(2)	0.001(2)
C(12)	4*e*	0.7537(6)	0.9298(3)	0.1210(4)	0.021(3)	0.015(3)	0.022(3)	0.003(2)	–0.001(2)	0.004(2)
I(1)	4*e*	0.79737(4)	0.49600(2)	0.08560(3)	0.0272(2)	0.0139(2)	0.0259(2)	0.0030(2)	0.0041(2)	0.0036(2)
I(2)	4*e*	0.34078(4)	0.71640(2)	–0.09376(3)	0.0157(2)	0.0150(2)	0.0277(2)	–0.0010(1)	–0.0001(2)	0.0003(2)
I(3)	4*e*	0.71013(4)	1.05059(2)	0.08915(3)	0.0381(2)	0.0146(2)	0.0303(2)	0.0053(2)	–0.0011(2)	0.0005(2)
I(4)	4*e*	0.99358(4)	0.23970(2)	0.22474(3)	0.0190(2)	0.0294(2)	0.0227(2)	–0.0009(2)	0.0014(2)	0.0022(2)
I(5)	4*e*	1.17709(4)	0.37990(2)	0.23333(3)	0.0179(2)	0.0247(2)	0.0173(2)	0.0049(2)	0.0007(2)	–0.0007(2)
I(6)	4*e*	1.38620(4)	0.50472(2)	0.23675(3)	0.0301(2)	0.0257(2)	0.0287(2)	–0.0033(2)	0.0068(2)	–0.0082(2)
N(1)	4*e*	0.8694(5)	0.8122(2)	0.0533(3)	0.018(2)	0.015(2)	0.018(2)	–0.004(2)	0.005(2)	–0.001(2)
O(1)	4*e*	0.5906(4)	0.8314(2)	–0.0407(3)	0.016(2)	0.011(2)	0.026(2)	–0.001(2)	–0.003(2)	0.002(2)

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